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(21) International Application Number: PCT/US89/04511 (22) International Filing Date: 12 October 1989 (12.10.89) (30) Priority data: 268,903 8 November 1988 (08.11.88) US (71) Applicant: PPG INDUSTRIES, INC. [US/US]; One PPG Place, Pittsburgh, PA 15272 (US). (72) Inventor: GOVINDAN, Cheruthur ; 996 Reedy Drive, Wadsworth, OH 44281 (US). (74) Agents: STEIN, Irwin, M.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al. (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).		Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: QUATERNARY AMMONIUM ANTISTATIC COMPOUNDS (57) Abstract Described are certain quaternary ammonium alkyl benzene sulfonate salts and certain quaternary ammonium alkane sulfonate salts, e.g., octyl dimethyl hydroxyethyl ammonium dodecyl benzene sulfonate and octyl dimethyl hydroxyethyl ammonium methane sulfonate which are useful as antistatic agents for synthetic polymer articles.		

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QUATERNARY AMMONIUM ANTISTATIC COMPOUNDS

2

DESCRIPTION OF THE INVENTION

4 The present invention relates to certain novel quaternary
ammonium sulfonate compounds and, more particularly, relates to the
6 use of such compounds as internal and external antistatic agents for
normally non-conducting organic materials. Still more particularly,
8 the present invention relates to shaped articles of synthetic and
naturally occurring organic polymers that have less than their normal
10 tendency to accumulate static charges of electricity.

Organic polymers, e.g., synthetic polymers, are essentially
12 electrical insulators, i.e., non-conductors of electricity. Articles
prepared from such polymers tend to develop electrostatic charges upon
14 their surfaces when they are in a dry state and are subjected to
friction during their production and finishing or during their
16 handling and use. Such static charges are undesirable for a number of
reasons. For example, surface static charges readily attract dust and
18 other contaminants, which are unsightly and difficult to clean. Often
the contaminants or static charges themselves cause processing or
20 handling problems. In certain cases, static charges may accumulate to
a level where an unpleasant electric shock is experienced when the
22 article is handled. Further, a high level of static charge on a
molded part covering sensitive electronic equipment can damage such
24 equipment.

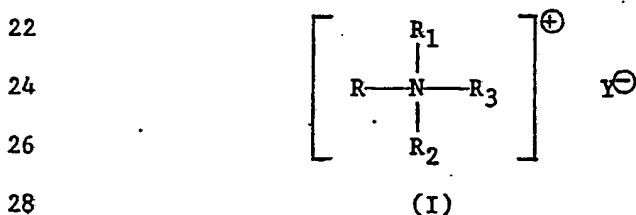
Articles prepared from non-conducting polymers may be surface
26 treated with a finish containing an antistatic agent; however, surface
treatments are less desirable than internally incorporated antistatic
28 agents due to a wearing away of the applied finish. Conversely,
antistatic agents that are incorporated within the shaped article by,
30 for example, blending the antistatic agent with the synthetic polymer
prior to forming of the article, are susceptible to decomposition as a
32 result of the high temperatures used to form the article, e.g., by
molding and extrusion. There is, therefore, a continuing need for
34 more thermally stable antistatic agents that may be used with
synthetic and naturally occurring polymers, and other naturally
36 occurring materials.

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The art has described the use of certain quaternary ammonium p-toluene sulfonate salts as antistatic agents. While some of these salts are relatively thermally stable, e.g., at temperatures of about 200°C., their performance as antistatic agents is not as efficacious as desired. In particular, the decay time of a charge applied to an article treated with the antistatic agent is too long. It is preferred that such decay times be less than 2 seconds, more preferably less than 1 second, and still more preferably less than 0.6 seconds.

It is an object of the present invention to provide novel antistatic agents for use internally or externally with formed synthetic materials, e.g., polymers, and other articles of manufacture to lessen the accumulation thereon of surface static charges.

It has now been discovered that certain quaternary ammonium sulfonate salts possess both thermal stability and markedly improved antistatic properties, i.e., electrostatic buildup and dissipation properties. Such properties may be measured by Federal Test Standard 101C, Method 4046, which measures the decay time for an applied charge of 5,000 volts. More particularly, the aforesaid quaternary salts may be represented by the following graphic formula I:



wherein R is a C₂-C₂₂ alkyl, preferably a C₈-C₁₈ alkyl, and R₁ is selected from the group consisting of C₁-C₂₂ alkyl and an alkyleneoxy radical, "Z", that may be represented by the formula, [CH₂-C(A)H-O]_xH, wherein A is hydrogen, methyl or ethyl, and x is an integer of from 1-5, e.g., hydroxyethyl, hydroxypropyl, hydroxybutyl, poly(ethyleneoxy) hydroxyethyl, poly(propyleneoxy) 2-hydroxypropyl, and poly(butyleneoxy) 2-hydroxybutyl. Preferably, R₁ is selected from the group consisting of C₁-C₃ alkyl or C₈-C₁₈ alkyl, e.g. methyl,

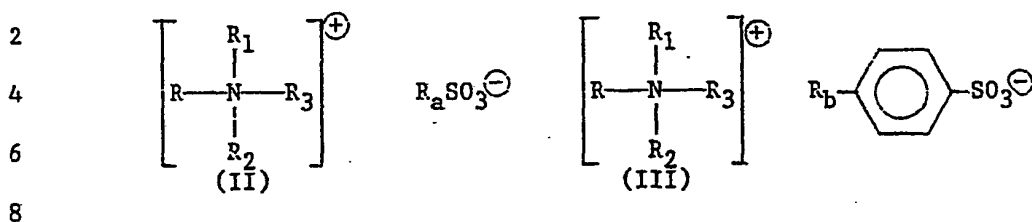
ethyl, n-propyl, isopropyl, octyl, decyl, dodecyl, hexadecyl, and 2 octadecyl, or the alkyleneoxy radical Z wherein A is hydrogen or methyl and x is 1 to 3. Still more preferably, R₁ is a C₁-C₃ alkyl or 4 alkyleneoxy radical Z wherein A is hydrogen and x is 1 to 2. When x is greater than 1, the sulfonate compound may be liquid, which makes 6 it easier to handle.

R₂ in the above graphic formula I is selected from the group 8 consisting of C₁-C₃ alkyl, e.g., methyl, ethyl, n-propyl and isopropyl, and the radical Z, wherein A and x are as defined with 10 respect to R₁. Alternatively R₁ and R₂ may also join together to form a six-membered morpholino group.

12 R₃ in the above graphic formula I is a group represented by the alkyleneoxy radical Z, wherein A and x are as defined with respect 14 to R₁; and Y is the anion, R'SO₃, wherein R' is a C₁-C₁₈ alkyl, preferably a C₁-C₂ alkyl, e.g., methyl and ethyl, or a C₈-C₁₈ 16 alkylphenyl, preferably a C₁₀-C₁₃ alkylphenyl. Preferably, the alkyl phenyl is a para-alkylphenyl.

18 With respect to R, R₁, and R', the term alkyl denotes a univalent, essentially saturated branched or straight chained alkyl 20 group. Representative of such alkyl groups include methyl, ethyl, propyl, butyl, pentyl, hexyl, isohexyl, heptyl, octyl, nonyl, decyl, 22 undecyl, dodecyl, cocoyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, soya, eicosyl and the like. When derived from 24 naturally occurring materials, the group R, R₁, and R' may contain a small amount of unsaturation and may be comprised of a mixture of 26 alkyl groups. For example, commercially available dodecyl benzene sulfonic acid is a benzene sulfonic acid in which the alkyl 28 substituent on the benzene ring is a mixture of C₁₀-C₁₃ alkyl groups, the nominal number of carbon atoms being about 12.

30 The aforescribed quaternary ammonium sulfonate salts may be more graphically illustrated by the following graphic formulae II and 32 III where R, R₁, R₂, and R₃ have the meanings described heretofore with respect to graphic formula I, R_a is a C₁-C₁₈ alkyl, e.g., C₁-C₂ 34 alkyl, and R_b is a C₈-C₁₈ alkyl, preferably a C₁₀-C₁₃ alkyl. As shown, R_b is a para-alkyl substituent, but it may be an ortho- or 36 meta-substituent.



Non-limiting examples of quaternary ammonium sulfonate compounds illustrated by graphic formula I include both the alkane sulfonate salts, such as methane sulfonate salts, and the alkyl benzene sulfonate salts, such as p-alkyl benzene sulfonate salts, that are described in Table I. There, R, R₁, R₂, R₃ and R_b are selected from the substituents tabulated therein:

TABLE 1

A. Methane Sulfonates

SUBSTITUENT

Compound/	R	R ₁	R ₂	R ₃
1	Octyl	Methyl	Methyl	Hydroxyethyl
2	Octyl	Ethyl	Ethyl	Hydroxyethyl
3	Soya	Methyl	Methyl	Hydroxyethyl
4	Decyl	Decyl	Methyl	Hydroxyethyl
5	Octyl	Methyl	Methyl	2-hydroxypropyl
6	Octyl	Methyl	Methyl	3-hydroxybutyl
7	Octyl	4-Morpholino		Hydroxyethyl
8	Octyl	Methyl	Hydroxyethyl	Hydroxyethyl
9	Decyl	Hydroxyethyl	Hydroxyethyl	Hydroxyethyl
10	Octyl	Hydroxyethyl	Hydroxyethyl	Hydroxyethyl
11	Octyl	Methyl	Methyl	Poly(ethyleneoxy) hydroxyethyl
12	Cocoyl	Hydroxyethyl	Hydroxyethyl	Hydroxyethyl

2

B. p-Alkyl Benzene Sulfonates

4	Compound/	R	R ₁	R ₂	R ₃	R _b
6						
	1	Octyl	Methyl	Methyl	Hydroxyethyl	Dodecyl
8	2	Octyl	Methyl	Methyl	2-hydroxypropyl	Dodecyl
	3	Octyl	Methyl	Methyl	3-hydroxybutyl	Dodecyl
10	4	Soya	Methyl	Methyl	Hydroxyethyl	Dodecyl
	5	Octyl	Octyl	Methyl	Hydroxyethyl	Dodecyl
12	6	Decyl	Decyl	Methyl	Hydroxyethyl	Dodecyl
14	7	Octyl	Methyl	Methyl	Poly(ethyleneoxy) hydroxyethyl	Dodecyl

16 Compound 1 in Table 1, Part A may be named octyl dimethyl
 2-hydroxyethyl ammonium methane sulfonate (where Y is methane
 18 sulfonate). Compound 1 in Table 1, Part B may be named octyl dimethyl
 2-hydroxyethyl ammonium p-dodecyl benzene sulfonate (where Y is
 20 dodecyl benzene sulfonate). Other sulfonate salts of the compounds
 from Table 1 may be similarly named by utilizing the appropriate
 22 IUPAC radical name for the designated substituents.

The quaternary ammonium sulfonate salts of graphic formula I
 24 may be used to minimize the accumulation of static electricity on
 non-conducting articles, e.g., articles prepared from synthetic
 26 polymers, by applying to the surface of or incorporating within the
 article effective antistatic amounts of at least one of the salts.
 28 Generally, the compounds of graphic formula I may be incorporated
 within the article in amounts of between about 0.5 and about 20 weight
 30 percent and preferably are used in amounts of between about 2 and
 about 6 weight percent, based on the weight of the dry, untreated
 32 article. When associated with a finish composition, the compounds of
 graphic formula I are generally present in amounts of from about 0.1
 34 to about 2, e.g., 0.5 to 1, weight percent.

When compounded into a shaped article of a synthetic polymer,
 36 the antistatic quaternary ammonium sulfonate salt will migrate or
 "bloom" to the surface of the article to provide an antistatic coating

thereon. Such a coating is more permanent than an externally
2 (topically) applied coating since the latter can be removed by wear,
wiping, washing, handling, movement in transit, etc. In contrast, if
4 the migrated layer of an internally compounded antistatic agent should
be removed during handling or processing, a new antistatic layer will
6 bloom to the surface.

To apply the antistatic compound topically to the surface of
8 an article, the antistatic compound is dissolved or dispersed in
water, lower alkanol, e.g., a C₁-C₄ alcohol, lubricating oil,
10 polymeric coating, other organic solvent, etc. and the resulting
"finish" containing the desired amount of antistatic compound applied
12 to the surface using conventional coating techniques, e.g., spraying,
dipping, wiping, etc., thereby to deposit an effective amount of
14 antistatic agent on the surface of the article.

In general, the antistatic compounds of graphic formula I are
16 thermally stable at temperatures in excess of 200°C. When heated to
temperatures up to about 275°C., weight losses of less than 5 weight
18 percent have been observed for compounds such as octyl dimethyl
hydroxyethyl ammonium methane sulfonate. The compounds may be solids,
20 liquids or low melting waxes, depending on the number of carbons in
the R, R₁, R₂ and R₃ alkyl groups. At the same time, these compounds
22 are more antistatic, i.e., exhibit shorter decay times, than sulfonate
salts currently in commercial use, e.g., p-toluene sulfonate salts.

24 When antistatic compounds are incorporated internally into an
article, the compound may be mixed in antistatic amounts with the
26 synthetic polymer or other material by conventional blending or mixing
equipment, e.g., Banbury mixers or other rubber and plastic processing
28 equipment, and the mixture formed into the article, e.g., by extrusion
or other molding procedure. Alternatively, a master batch of the
30 polymer and antistatic compound may be prepared and the master batch
added in antistatic amounts to synthetic polymer that is to be formed
32 into an article, thereby to provide the desired antistatic amount of
antistatic compound within the article. A master batch may contain
34 between about 10 and about 25 percent by weight of the antistatic
compound.

The compounds of graphic formula I may be used with
2 conventional synthetic polymers utilized to prepare formed articles.

The compatibility of the antistatic compounds with a particular
4 synthetic polymer may be readily determined by those skilled in the
art. Antistatic compounds of graphic formula I may be used in a wide
6 spectrum of substrate shapes, such as fibers (woven and nonwoven),
sheets, films and molded or extruded articles. Such articles may be
8 prepared from thermoplastic or thermosetting polymers or copolymers
(including terpolymers).

10 Non-limiting examples of synthetic polymers from which formed
articles may be prepared include polyolefins, such as polyethylene,
12 polypropylene and polyisobutylene, styrene resins such as polystyrene,
poly(chlorostyrene), styrene-acrylonitrile copolymers, poly(styrene-
14 acrylonitrile-butadiene) terpolymers (ABS resins) and high impact
polystyrene (HIPS), polyesters such as poly(methylacrylate),
16 poly(methylmethacrylate) and poly(vinylacetate), ethylene glycol-
terephthalic acid polymers, polycarbonates, polyamides such as nylon
18 and Kevlar® type polyamides, polyacetals such as poly(vinylbutyral),
phenol-formaldehyde resins, vinyl resins, such as poly(vinyl
20 chloride), poly(vinylidene chloride), polytrifluorochloroethylene,
copolymers of vinyl chloride with vinyl acetate, vinylidene chloride,
22 or acrylonitrile, polyurethanes, and poly(phenylene ether) resins.

Mixtures of the aforesaid polymers may also be used, e.g., polymer
24 alloys.

In addition, the compounds of graphic formula I may be used
26 with natural materials or mixtures of natural and synthetic materials,
e.g., rayon, acetate, rayon-cellulosic materials such as cellulose
28 acetate-propionate, cellulose-butyrate, cotton, linen, jute, ramie,
wool, mohair and glass, e.g., fiberglass and fiberglass insulation.
30 The textile materials may take any form, including individual fibers,
woven material such as fabrics, cloth, carpets, rugs and upholstery
32 and non-woven materials such as felts, bats and mats. In the case of
fiberglass strand or fiberglass insulation, the compounds of graphic
34 formula I may be applied topically as a finish or as part of a sizing
composition.

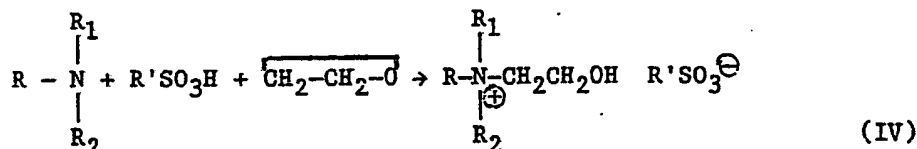
The compounds of graphic formula I may be prepared by reacting approximately equal molar amounts of the tertiary amine and an ester of alkane sulfonic acid or alkyl benzene sulfonic acid in the presence of a solvent, e.g., water, lower alkanols, e.g., C₁-C₄ alkanols, or acetone, at temperatures of from about 25°C. to about 250°C., e.g., from about 65 to 80°C., under a slight positive nitrogen pressure. Preferably, the compounds of graphic formula I may be prepared more readily by reacting the corresponding tertiary amine, corresponding sulfonic acid, e.g., methane sulfonic acid, and alkylene oxide, e.g., ethylene oxide, in accordance with the following equation IV.

12

14

16

18



Quaternization of tertiary amines with alkylene oxide is preferably performed in the presence of a small amount of amine catalyst and at elevated pressures, the later accelerating the take-up of the alkylene oxide. Quaternary amines containing poly(alkylene oxide), e.g., poly(ethylene oxide) groups may preferably be prepared in the presence of a slight excess of the amine, an excess of alkylene oxide and at elevated pressures, which may be from about 10 to about 100 pounds per square inch (.07-0.7 MPa).

The present invention is more particularly described in the following examples which are intended as illustrative only since numerous modifications and variations will be apparent to those skilled in the art.

32

Example 1

118.0 grams (0.75 moles) of n-octyl dimethylamine were neutralized with a solution of 72.0 grams (0.75 moles) of methane sulfonic acid in 100 milliliters of water. The temperature of the

- 9 -

resulting mixture rose to about 80-90°C. and thereafter was cooled to about 40°C. The reaction mixture was charged to an autoclave and, after thoroughly flushing the system with nitrogen, the autoclave was sealed and pressurized with nitrogen to 20 pounds per square inch (psig) (0.1 MPa). The contents of the autoclave were heated to about 70°C. and 62.0 grams (1.4 moles) of ethylene oxide charged to the autoclave. The contents of the autoclave were stirred for 1 hour while maintaining the temperature at 70°C. Thereafter, the autoclave was flushed with nitrogen and the reaction mixture cooled. The pH of the cooled solution in the autoclave was determined to be about 10.5 and subsequently adjusted to about 4.7 using methane sulfonic acid and a 50 percent sodium hydroxide aqueous solution. 50.0 grams of the solution in the autoclave were stripped under vacuum; the residue dissolved in an acetone-ether solution; and the solution decolorized with charcoal. The decolorized mixture was filtered and concentrated to obtain 31.5 grams of a clear liquid that solidified on standing. The product, n-octyl dimethyl hydroxyethyl ammonium methane sulfonate, was confirmed by discharge ionization secondary ion mass spectrometry (DISIMS).

20

Example 2

62.0 grams (0.28 moles) of n-octyl diethanol amine were neutralized with a solution of 27.0 grams (0.28 moles) of methane sulfonic acid in 100 milliliters of water. The pH of the mixture was determined to be about 5.3 and was adjusted subsequently to 6.3 with octyl dimethyl amine. 50 milliliters of water were added to the neutralized mixture and the resulting solution charged to an autoclave, which was first flushed with nitrogen and then pressurized with nitrogen to 20 psig (0.1 MPa). The contents of the autoclave were heated to 65°C. and 25.0 grams (0.37 moles) of ethylene oxide added thereto over a period of 30 minutes. After addition of the ethylene oxide, the nitrogen pressure was increased to 100 pounds psig (0.7 MPa) and the reaction mixture stirred for 2 hours. The reaction mixture was then cooled, the autoclave flushed with nitrogen, and the contents of the autoclave stripped under vacuum to obtain 108 grams of a viscous liquid. The product, n-octyl tris(hydroxyethyl) ammonium methane sulfonate, was confirmed by DISIMS spectrometry.

2

Example 3

To a solution of 123.3 grams (0.41 moles) of soya dimethyl amine in 200 milliliters of isopropanol were added with stirring 132.0 grams of dodecyl benzene sulfonic acid. The temperature of the mixture rose to about 50°C. The pH of the mixture was determined to be about 1.8. The mixture was charged to an autoclave, which was sealed and pressurized with nitrogen to 20 psig (0.1 MPa). The mixture was heated to 70°C. and 35.0 grams (0.80 moles) of ethylene oxide added to the reactor over a period of 30 minutes. The mixture was stirred overnight while maintaining it at a temperature of 70°C. The pressure was then released and the contents of the autoclave cooled. Isopropanol was stripped from the crude reaction product on a rotary evaporator to obtain 252 grams of a slight yellow paste. The structure of the product was determined by mass spectroscopy to be a mixture corresponding to n-soya dimethyl hydroxyethyl ammonium dodecyl benzene sulfonate.

18

Example 4

To a solution of 160.0 grams (0.5 moles) of dodecyl benzene sulfonic acid in 150 milliliters of ethanol were added with stirring 78.3 grams (0.5 moles) of octyl dimethyl amine. The mixture was charged to an autoclave which was pressurized with nitrogen to a pressure of 20 psig (0.1 MPa.) The mixture was heated to 65°C. and 28.0 grams (0.64 moles) of ethylene oxide added with stirring to the autoclave over a period of 30 minutes. The mixture was then stirred for 2 hours while maintaining it at a temperature of 65°C. The pressure in the autoclave was released, the contents cooled and the ethanol solvent stripped in vacuo to obtain 244.0 grams of a thick liquid.

Since no weight gain was observed, the liquid product was redissolved in 200 milliliters of isopropanol and charged to an autoclave. The contents of the autoclave were warmed to 80°C. and the autoclave pressurized with nitrogen to 20 psig (0.1 MPa). Ethylene oxide (44.0 grams, 1.0 mole) was added to the autoclave over a period of 30 minutes and the autoclave contents stirred overnight while

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maintaining the contents of the autoclave at a temperature of 80°C. 2 and at a pressure of 100 psig (0.7 MPa). The pressure was released and the reaction product cooled. The isopropanol solvent was stripped 4 in vacuo to obtain 262.0 grams of a light yellow gel. This product was found to be octyl dimethyl hydroxyethyl ammonium dodecyl benzene 6 sulfonate by mass spectroscopy.

8

Example 5

To a solution of 160.0 grams of dodecyl benzene sulfonic acid 10 in 100 milliliters of isopropanol were added 79.5 grams of octyl dimethyl amine. The mixture was charged to an autoclave which was 12 pressurized with nitrogen to a pressure of 20 psig (0.1 MPa). The mixture was warmed to 80°C. and 35.0 grams of propylene oxide added 14 with stirring to the autoclave over a period of about 30 minutes. The mixture was stirred overnight while maintaining it at a temperature of 16 80°C. In the morning the autoclave pressure had dropped to 10 psig (0.07 MPa), which indicated that the autoclave seal had a leak.

18 The solvent was stripped from the mixture and the residue (256.8 grams) redissolved in 150 milliliters of isopropanol and the 20 solution charged to the autoclave. Propylene oxide (30.0 grams) was added to the autoclave, the contents warmed to 80°C. and the autoclave 22 pressurized to 30 psig (0.2 MPa) with nitrogen. The pressure dropped to 20 psig (0.1 MPa) in 1 hour. The mixture was stirred overnight at 24 a temperature of 60°C. In the morning the pressure was found to be about 5 psig (0.03 MPa). The mixture was cooled and the solvent 26 stripped on a rotary evaporator. The residue (270.5 grams) was the product octyl dimethyl 2-hydroxypropyl ammonium dodecyl benzene 28 sulfonate, which was confirmed by mass spectroscopy.

30

Example 6 (Comparative)

157.3 grams of octyl dimethyl amine were charged to an 32 autoclave and neutralized with a solution of 189.5 grams of p-toluene sulfonic acid in 100 milliliters of water. The temperature of the 34 mixture was about 60°C. at the end of the neutralization step. The autoclave was sealed, flushed twice with nitrogen and pressurized to

- 12 -

25 psig (0.2 MPa) with nitrogen. The mixture was warmed to 75-80°C. 2 and 46.0 grams of ethylene oxide added to the autoclave over about 1 hour. The mixture was stirred at 70°C. for 1 hour.

4 The pressure in the autoclave was released and the product recovered. A portion of the product was stripped in vacuo and the 6 residue washed with ether. A white powder product was obtained by filtration. Mass spectroscopy confirmed the product to be octyl 8 dimethyl hydroxyethyl ammonium p-toluene sulfonate.

10 Example 7

An aqueous solution containing 0.09 weight percent of the 12 compound of Example 1 was prepared. A 3 1/2 inch (8.9 cm) x 5 inch (12.7 cm) swatch of an acrylic fabric obtained from Testfabrics Inc. 14 was immersed in 100 grams of the aqueous solution for 30 seconds.

Excess solution was squeezed from the swatch using an Atlas laboratory 16 wringer. The swatches were air dried and then conditioned for 24 hours in a controlled humidity chamber maintained at 15 percent 18 relative humidity. This procedure was repeated with the compounds of Examples 2, 4, 5 and 6, and with the commercial antistatic compound 20 Hexcel®106G. Electrostatic properties of the swatches were measured in accordance with Federal Test Standard 101C, Method 4046 by applying 22 a charge of 5,000 volts to each of the acrylic fabric swatches and measuring the time in seconds required for the charge to decay to 0 24 volts with an Electrotech Systems static decay meter, Model 406C.

Results are tabulated in Table 2.

26

Table 2

28

<u>Example (Compound)</u>	<u>1</u>	<u>2</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>Hexcel 106G*</u>
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30

Decay Time (sec)	0.3	0.5	0.6	0.9	10	1.7
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32 * octyl methyl di(hydroxyethyl) ammonium p-toluene sulfonate

34 The data of table 2 show that compounds of graphic formula I, e.g., compounds of Examples 1,2,4 and 5 have excellent antistatic 36 properties - exhibiting superior decay times compared to the compound

- 13 -

of Example 6 (octyl dimethyl hydroxyethyl p-toluene sulfonate) and 2 significantly improved decay times compared to the commercial antistatic product Hexcel® 106G.

4

Example 8

6 Noryl® N-190 modified poly(phenylene oxide) resin and 2 weight percent of antistatic compound corresponding to Example 1 were 8 blended for 5 minutes in a Brabender mixer (100 rpm) at 210°C. The resulting mixture was compression molded at 440°F. (227°C.) into a 10 flat plaque about 55 mils thick. The aforesaid procedure was repeated except that 5 weight percent of the antistatic compound was used.

12 Five inch (12.7 cm) square discs cut from each of the plaques were conditioned for 24 hours in a controlled humidity chamber 14 maintained at 15 percent relative humidity. The surface resistivity and electrostatic property (decay time) of the discs were measured 16 using the test method described in Example 7. Results are tabulated in Table 3.

18

Example 9

20 The procedure of Example 8 was repeated using the compound of Example 4. Results are tabulated in Table 4.

22

Example 10

24 High impact polystyrene (HIPS-Mobil polystyrene 4226) and 2 weight percent of antistatic compound corresponding to Example 1 were 26 blended for 3 minutes in a Brabender mixer (100 rpm) at 210°C. The resulting mixture was compression molded at 420°F. (216°C.) into a 28 flat plaque about 55 mils thick. The procedure was repeated except that 5 weight percent of the antistatic compound was used. The 30 surface resistivity and electrostatic property of each of the plaques were tested in the manner described in Example 8. Results are 32 tabulated in Table 3.

34

Example 11

The procedure of Example 10 was repeated using the compound 36 of Example 4. Results are tabulated in Table 4.

2

Example 12

A poly(vinyl chloride) plastisol resin was prepared in the following manner. 92 parts of Geon 173 dispersion resin and 8 parts of Borden 260 ss blending resin were mixed in a blender. 49 parts of dioctyl phthalate and 4 parts of Synpron 1363 thermal stabilizer were mixed and the mixture added with stirring slowly to the blender. After all of the dioctyl phthalate/stabilizer blend had been added, the resulting mixture was stirred for an additional 5 minutes. 0.75 grams of the antistatic compound corresponding to Example 1 was added to 14.25 grams of the plastisol resin and the mixture stirred well. A 10 mil film was drawn down on a 7 inch (17.8 cm) square piece of cardboard and the film cured at 193°C. for 2 minutes. The surface resistivity and electrostatic property of the film were measured using the method described in Example 7. Results are tabulated in Table 3.

16

Example 13

The procedure of Example 12 was repeated using the compound of Example 4. Results are tabulated in Table 4.

20

TABLE 3PLASTIC RESIN

<u>Antistat. Wt%</u>	<u>NORYL</u>		<u>HIPS</u>		<u>PVC</u>
	<u>2</u>	<u>5</u>	<u>2</u>	<u>5</u>	<u>PLASTISOL</u> <u>5</u>
Decay Time, Secs	1.2	0.2	0.9	0.03	0.07
Resistivity, ohm/sq	3×10^{10}	5×10^{11}	2×10^{11}	3×10^9	1.5×10^{10}

The data of Table 3 shows that the compound of Example 1 exhibits excellent antistatic properties - showing decay times of less than 1 second for each of the plastic resins at the 5 percent level.

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TABLE 4

PLASTIC RESIN

<u>Antistat. Wt%</u>	<u>NORYL</u>		<u>HIPS</u>		<u>PVC</u>
	<u>2</u>	<u>5</u>	<u>2</u>	<u>5</u>	<u>PLASTISOL</u>
Decay Time, secs	1.8	0.7	3.1	1.1	0.5
Resistivity, ohm/sq	8×10^{11}	2×10^{11}	1×10^{12}	4×10^{11}	5×10^{10}

The data of Table 4 show that the compound of Example 4 has good antistatic properties at a 2 weight percent level and very good antistatic properties at a 5 weight percent level - showing decay times of about 1 second or less for the later level of compounding.

Example 14

To a solution of 48.0 grams of 98% methane sulfonic acid in 150 milliliters of water were added with stirring 79.0 grams of octyl dimethyl amine. The temperature of the reaction was maintained at 60-65°C. The pH of the resulting solution was determined to be 1.5 and was subsequently adjusted to 6 with additional octyl dimethyl amine. The solution was charged to an autoclave, which was pressurized with nitrogen to 30 psig (0.2 MPa). The contents in the autoclave were heated to 70°C. and 48.0 grams of ethylene oxide were added over a period of 30 minutes. Thereafter the reaction mixture was stirred at 70°C. for 1.5 hours. The pressure in the autoclave was released and the reaction product stripped in vacuo to obtain 174.0 grams of a liquid product which remained liquid even on prolonged storage. The product was identified by mass spectroscopy to correspond to the products $C_8H_{17}N(CH_3)_2(CH_2CH_2O)_xHCH_3SO_3$, wherein x was 1, 2 and 3.

Example 15

A solution of 68.5 grams of 70% methane sulfonic acid in 150 milliliters of water were neutralized with 107.0 grams of dodecyl dimethyl amine at 80-90°C. The pH of the neutralized solution was determined to be 1.8, which was subsequently adjusted to 5 with additional dodecyl dimethyl amine. The resulting solution was charged

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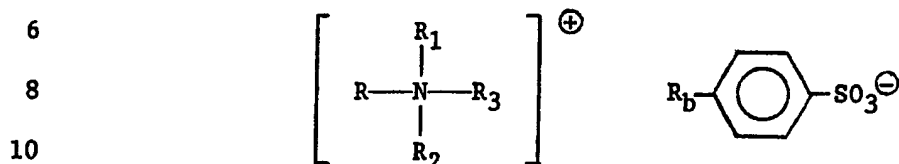
to an autoclave, which was pressurized with nitrogen to 20 psig (0.1
2 MPa), and the solution heated to 70°C. 68.0 grams of ethylene oxide
was added to the autoclave over 45 minutes. After addition of the
4 ethylene oxide, the reactor contents were stirred for one hour while
maintaining it at 70°C. Pressure in the autoclave was released and
6 the liquid product stripped in vacuo to obtain 224.0 grams of a liquid
product. Mass spectroscopy showed the product to be a mixture of the
8 mono- and diethoxylated quaternary amine, i.e., $C_{12}H_{25}N(CH_3)_2$
 $(CH_2CH_2O)_xH$, wherein x is 1 and 2.

10 Although the present invention has been described with
reference to specific details of certain embodiments thereof, it is
12 not intended that such details should be regarded as limitations upon
the scope of the invention except as and to the extent that they are
14 included in the accompanying claims.

CLAIMS

2

1. A quaternary ammonium compound represented by the graphic
4 formula:



wherein R is a C₂-C₂₂ alkyl, R₁ is selected from the group consisting
12 of C₁-C₂₂ alkyl and an alkyleneoxy radical represented by the formula
-CH₂-C(A)H-O]_xH, R₂ is selected from the group consisting of C₁-C₃
14 alkyl, and the alkyleneoxy radical, -CH₂-C(A)H-O]_xH, or R₂ may join
together with R₁ to form a morpholino group, R₃ is an alkyleneoxy
16 radical represented by the formula -CH₂-C(A)H-O]_xH, R_b is a C₈-C₁₈
alkyl, A is selected from the group consisting of hydrogen, methyl and
18 ethyl, and x is an integer of from 1 to 5.

20 2. The quaternary ammonium compound of claim 1 wherein R is
a C₈-C₁₈ alkyl, R₁ is selected from the group consisting of C₁-C₃
22 alkyl, C₈-C₁₈ alkyl and the alkyleneoxy radical, -CH₂-C(A)H-O]_xH, R₂
is selected from the group consisting of C₁-C₃ alkyl and
24 -CH₂-C(A)H-O]_xH, R₃ is -CH₂-C(A)H-O]_xH, R_b is a C₁₀-C₁₃ alkyl, A is
hydrogen or methyl and x is an integer of from 1 to 3.

26

3. The quaternary ammonium compound of claim 2 wherein R₁ is
28 selected from the group consisting of C₁-C₃ alkyl and
-CH₂-C(A)H-O]_xH.

30

4. The quaternary ammonium compound of claim 2 wherein R₁
32 and R₂ are each selected from the group consisting of C₁-C₂ alkyl and
-CH₂-C(A)H-O]_xH, R₃ is -CH₂-C(A)H-O]_xH, and A is hydrogen.

34

5. The quaternary ammonium compound of claim 2 wherein R_1 and R_2 are each C_1-C_2 alkyl and R_3 is the radical, $\{CH_2-C(A)H-O\}_xH$, and A is hydrogen or methyl.

4

6. The quaternary ammonium compound of claim 2 wherein R_1 , R_2 and R_3 are each $\{CH_2-C(A)H-O\}_xH$, and A is hydrogen.

7. The quaternary ammonium compound of claim 2 wherein R_1 is C_1-C_2 alkyl and R_2 and R_3 are each $\{CH_2-C(A)H-O\}_xH$, and A is hydrogen.

10

8. The quaternary ammonium compound of claim 5 wherein R is octyl, R_1 and R_2 are each methyl, R_3 is the radical, $\{CH_2-C(A)H-O\}_xH$, A is hydrogen or methyl, x is an integer of from 1 to 3, and R_b is a $C_{10}-C_{13}$ alkyl.

9. The quaternary ammonium compound of claim 8 wherein A is hydrogen and R_b is dodecyl.

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10. The quaternary ammonium compound of claim 8 wherein A is methyl and R_b is dodecyl.

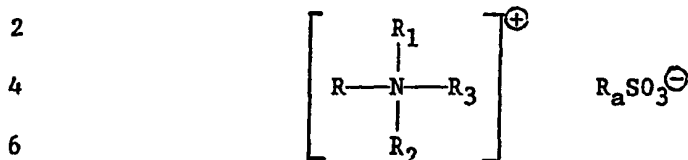
11. The quaternary ammonium compound of claim 5 wherein R is soya, R_1 and R_2 are each methyl, R_3 is the radical, $\{CH_2-C(A)H-O\}_xH$, A is hydrogen, x is an integer of from 1 to 3, and R_b is dodecyl.

12. The quaternary ammonium compound of claim 5 wherein R is octyl, R_1 is methyl, R_2 and R_3 are each the radical, $\{CH_2-C(A)H-O\}_xH$, wherein A is hydrogen, x is an integer of from 1 to 3 and R_b is a $C_{10}-C_{13}$ alkyl.

30

13. The quaternary ammonium compound of claim 12 wherein R_b is dodecyl.

14. A quaternary ammonium compound represented by the graphic formula:



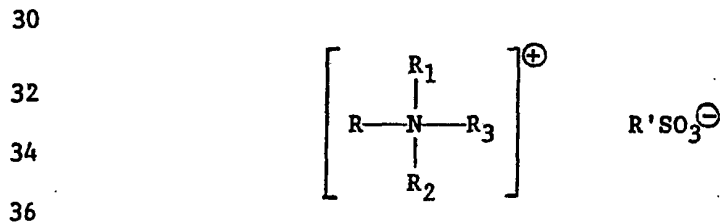
8 wherein R is octyl, R_1 and R_2 are each selected from the group
 consisting of C_1 - C_2 alkyl and the radical, $\{CH_2-C(A)H-O\}_xH$, R_3 is the
 10 radical, $\{CH_2-C(A)H-O\}_xH$, R_a is C_1 - C_2 alkyl, A is selected from the
 group consisting of hydrogen, methyl and ethyl, and x is an integer of
 12 from 1 to 3.

14 15. The quaternary ammonium compound of claim 14 wherein R_1
 and R_2 are each methyl, R_a is methyl, and A is hydrogen.

16 16. The quaternary ammonium compound of claim 14 wherein R_1
 18 is methyl, R_2 and R_3 are each the radical, $\{CH_2-C(A)H-O\}_xH$, R_a is
 methyl and A is hydrogen.

20 17. The quaternary ammonium compound of claim 14 wherein R_1 ,
 22 R_2 and R_3 are each the radical, $\{CH_2-C(A)H-O\}_xH$, R_a is methyl and A is
 hydrogen.

24 18. An organic article having antistatic properties
 26 comprising an organic material which in a dry state has a tendency to
 accumulate static charges of electricity thereon and an antistatically
 28 effective amount of a quaternary ammonium compound represented by the
 graphic formula:



wherein R is a C_2 - C_{22} alkyl, R_1 is selected from the group consisting

of C₁-C₂₂ alkyl and an alkyleneoxy radical represented by the formula
2 {CH₂-C(A)H-O}_xH, R₂ is selected from the group consisting of C₁-C₃
alkyl and the alkyleneoxy radical, {CH₂-C(A)H-O}_xH, or R₂ may join
4 together with R₁ to form a morpholino group, R₃ is an alkyleneoxy
radical represented by the formula, {CH₂-C(A)H-O}_xH, R' is selected
6 from the group consisting of C₁-C₁₈ alkyl and C₈-C₁₈ alkylphenyl, A is
selected from the group consisting of hydrogen, methyl and ethyl, and
8 x is an integer of from 1 to 5.

10 19. The article of claim 18 wherein R is a C₈-C₁₈ alkyl, R₁
is a C₁-C₃ alkyl, C₈-C₁₈ alkyl, or the radical, {CH₂-C(A)H-O}_xH, R₂ is
12 selected from the group consisting of C₁-C₃ alkyl and the radical,
{CH₂-C(A)H-O}_xH, A is hydrogen or methyl and x is an integer of from 1
14 to 3.

16 20. The article of claim 19 wherein the article is a
synthetic polymer.

18

21. The article of claim 20 wherein the synthetic polymer is
20 selected from the group consisting of polyolefins, styrene resins,
polyesters, ethylene glycol-terephthalic acid polymers,
22 polycarbonates, polyamides, polyacetals, vinyl resins, poly(phenylene
ether) resins, and mixtures of such polymers.

24

22. The article of claim 21 wherein the quaternary ammonium
26 compound is associated with the article in amounts of between about
0.5 and about 20 weight percent.

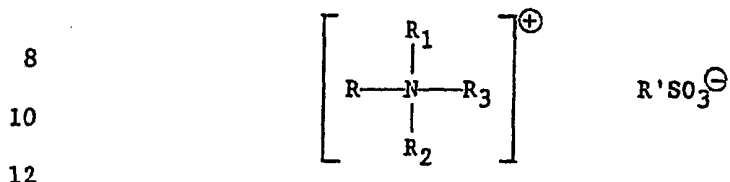
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23. The organic article of claim 21 wherein R is octyl, R₁
30 and R₂ are each C₁-C₃ alkyl or the radical, {CH₂-C(A)H-O}_xH, R₃ is the
radical {CH₂-C(A)H-O}_xH, R' is C₁-C₂ alkyl or C₁₀-C₁₃ alkylphenyl, A
32 is hydrogen or methyl and x is an integer of from 1 to 3.

34 24. The organic article of claim 23 wherein R₁ and R₂ are
each methyl and n is 1.

36

25. A method for treating an article formed of a material
2 which in a dry state has a tendency to accumulate static charges of
electricity thereon, which comprises applying to the surface of said
4 article a finish composition containing from about 0.1 to about 2
weight percent of a quaternary ammonium compound represented by the
6 graphic formula:



wherein R is a C₂-C₂₂ alkyl, R₁ is selected from the group consisting
14 of C₁-C₂₂ alkyl and an alkyleneoxy radical represented by the formula
-[CH₂-C(A)H-O]_xH, R₂ is selected from the group consisting of C₁-C₃
16 alkyl and the radical, [CH₂-C(A)H-O]_xH, or R₂ may join together with
R₁ to form a morpholino group, R₃ is an alkyleneoxy radical
18 represented by the formula, [CH₂-C(A)H-O]_xH, R' is selected from the
group consisting of C₁-C₁₈ alkyl and C₈-C₁₈ alkyl phenyl, A is
20 selected from the group consisting of hydrogen, methyl and ethyl, and
x is an integer of from 1 to 5.

22

26. The method of claim 25 wherein R is a C₈-C₁₈ alkyl, R₁ is
24 a C₁-C₃ alkyl, C₈-C₁₈ alkyl, or the radical, [CH₂-C(A)H-O]_xH, R₂ is
selected from the group consisting of C₁-C₃ alkyl and the radical,
26 [CH₂-C(A)H-O]_xH, A is hydrogen or methyl and x is an integer of from 1
to 3.

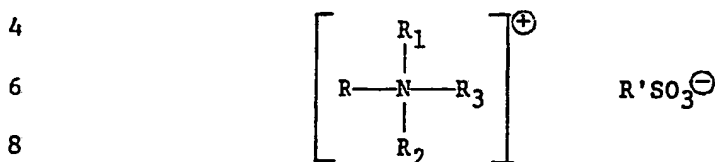
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27. The method of claim 26 wherein the article is a synthetic
30 polymer selected from the group consisting of polyolefins, styrene
resins, polyesters, ethylene glycol-terephthalic acid polymers,
32 polycarbonates, polyamides, polyacetals, vinyl resins and
poly(phenylene ether) resins, and mixtures of such polymers.

34

28. A synthetic polymer composition having antistatic
36 properties comprising a synthetic polymer having incorporated therein

an antistatically effective amount of a quaternary ammonium compound
2 represented by the graphic formula:



10 wherein R is a C₂-C₂₂ alkyl, R₁ is selected from the group consisting
of C₁-C₂₂ alkyl and an alkyleneoxy radical represented by the formula
12 $\text{-(CH}_2\text{-C(A)H-O)}_x\text{H}$, R₂ is selected from the group consisting of C₁-C₃
alkyl and the radical, $\text{-(CH}_2\text{-C(A)H-O)}_x\text{H}$, or R₂ may join together with
14 R₁ to form a morpholino group, R₃ is a radical represented by the
formula, $\text{-(CH}_2\text{-C(A)H-O)}_x\text{H}$, R' is selected from the group consisting of
16 C₁-C₁₈ alkyl and C₈-C₁₈ alkyl phenyl, n is a number of from 1 to 3 and
x is a number of from 1 to 5.

18

29. The polymer composition of claim 28 wherein the synthetic
20 polymer is selected from the group consisting of polyolefins, styrene
resins, polyesters, ethylene glycol-terephthalic acid polymers,
22 polycarbonates, polyamides, polyacetals, vinyl resins, poly(phenylene
ether) resins, and mixtures of such polymers.

24

30. The polymer composition of claim 29 wherein the
26 quaternary ammonium compound is incorporated into the synthetic
polymer in amounts of between about 0.5 and about 20 weight percent.

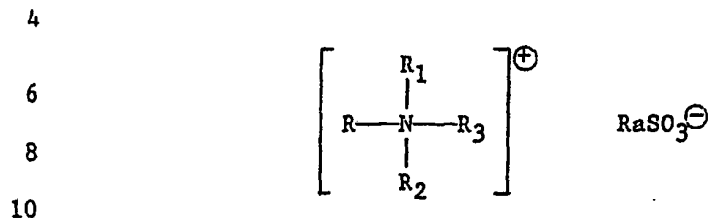
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31. The polymer composition of claim 30 wherein R is octyl,
30 R₁ and R₂ are each C₁-C₃ alkyl or the radical, $\text{-(CH}_2\text{-C(A)H-O)}_x\text{H}$, R₃ is
the radical, $\text{-(CH}_2\text{-C(A)H-O)}_x\text{H}$, R' is C₁-C₂ alkyl or C₁₀-C₁₃
32 alkylphenyl, A is hydrogen or methyl and x is an integer of from 1 to
3.

34

32. The polymer composition of claim 31 wherein R₁ and R₂ are
36 each methyl and A is hydrogen.

2 33. A quaternary ammonium compound represented by the
 4 graphic formula:



wherein R is selected from the group consisting of soya, cocoyl and
 12 decyl, R_1 and R_2 are each selected from the group consisting of C_1 - C_2
 alkyl and the radical, $[-CH_2-C(A)H-O]_xH$, R_3 is the radical
 14 $[-CH_2-C(A)H-O]_xH$, Ra is C_1 - C_2 alkyl, A is selected from the group
 consisting of hydrogen, methyl and ethyl, and x is an integer of from
 16 1 to 3.

18 34. The quaternary ammonium compound of claim 33 wherein R
 is soya, R_1 and R_2 are each methyl, Ra is methyl and A is hydrogen.

20

